CHAPTER 5

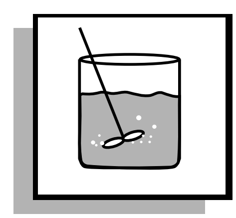
Wastewater Treatment Technologies

Wastewater treatment technologies are used by PFPR facilities to remove or destroy pesticide active ingredients and other pollutants in facility wastewater. The treated effluent may be reused in PFPR operations or may be discharged to a receiving stream or treatment facility (such as a publicly owned treatment works (POTW)). This chapter describes five cost-effective technologies that remove or destroy pesticide active ingredients and priority pollutants, and references other technologies that also effectively treat PFPR wastewaters. A list of documents that contain more detailed information on these technologies is included at the end of this chapter.

The technologies presented in this chapter have been identified through sampling visits to PFPR and pesticide manufacturing facilities and through EPA-sponsored treatability tests. The implementation of these, or equivalent, technologies has allowed PFPR facilities to reuse a greater percentage of wastewater in their operations without risking the quality of their final products. Additionally, by implementing these technologies, these facilities are able to discharge effluents that might otherwise require disposal.

Pretreatment Technologies

Emulsion Breaking



Many pesticide products are formulated by mixing pesticide active ingredients with inert materials (e.g., surfactants, emulsifiers, petroleum hydrocarbons) to achieve specific application characteristics. When these "inerts" mix with water, emulsions may form. These emulsions reduce the performance efficiency of many treatment unit operations, such as chemical oxidation and activated carbon adsorption. In many situations, emulsion breaking is a necessary pretreatment step to facilitate the removal of pollutants from PFPR wastewaters. Although emulsion breaking is a pretreatment step, its importance in the treatment of PFPR wastewaters can make it a major part of the technology train for treating PFPR wastewaters.

Types of Emulsions

- O/W Emulsion - a hydrophobic solvent, such as oil, dispersed in an aqueous medium
- W/O Emulsion - an aqueous medium dispersed in a hydrophobic solvent, such as oil.

Facilities can break these emulsions through several methods. Temperature control and acid addition are common in the PFPR industry and are discussed in more detail below. Other methods of emulsion breaking, such as chemically assisted clarification, are not discussed in this manual. Additional information on these methods may be found in the Final PFPR Technical Development Document (EPA 821-R-96-019).

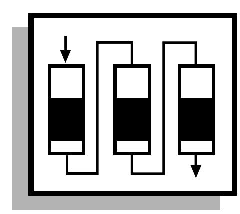
Temperature control and acid addition are simple, inexpensive methods of breaking emulsions in a variety of PFPR wastewaters. Acid (e.g., sulfuric acid) added to emulsified wastewater dissolves the solid materials that hold the emulsions together. The demulsified oil floats because of its lower specific gravity and can be skimmed off the surface, leaving the wastewater ready for subsequent treatment. The demulsification also causes suspended solids with a higher specific gravity to settle out of the wastewater. Heating the emulsion lowers the viscosities of the oil and water and increases their apparent specific gravity differential. The oil, with a significantly lower apparent specific gravity, rises to the surface of the wastewater. Heating the wastewater also increases the kinetic energy of the individual molecules in the wastewater, causing the molecules to collide with each other more frequently. The increased number of molecule collisions aids in breaking the film present between the oil and the water. Once freed from the water, the oil rises, where it can be skimmed from the surface of the wastewater. Emulsion breaking on PFPR wastewater has been effective in EPA-sponsored treatability tests when conducted at pH 2 and 60°C.

Other Pretreatment Technologies

In addition to emulsion breaking, a variety of other technologies effectively pretreat PFPR wastewater, including membrane filtration (ultrafiltration), chemically assisted clarification, and settling. Although these technologies are not discussed here, additional information on the treatment tests conducted by EPA using these technologies can be found in the Final PFPR Technical Development Document (EPA 821-R-96-019) and in the administrative record supporting the final PFPR rulemaking.

Treatment Technologies

Activated Carbon Adsorption



Activated carbon effectively removes organic constituents from wastewater through the process of adsorption. The term "activated carbon" refers to carbon materials, such as coal or wood, that are processed through dehydration, carbonization, and oxidation to yield a material that is highly adsorbent due to a large surface area and high number of internal pores per unit mass. As wastewater flows through a bed of carbon materials, molecules that are dissolved in the water may become trapped in these pores.

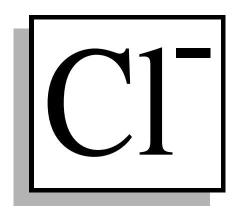
In general, organic constituents (including many pesticide active ingredients) with certain chemical structures (such as aromatic functional groups), high molecular weights, and low water solubilities are amenable to activated carbon adsorption. These constituents adhere to the stationary carbon material, so the wastewater leaving the carbon bed has a lower concentration of pesticide than the wastewater entering the carbon bed. Eventually, as the pore spaces in the carbon become filled, the carbon becomes exhausted and ceases to adsorb contaminants. Spent carbon may be regenerated or disposed of; the choice is generally determined by cost and/or other regulatory factors (e.g., RCRA).

Carbon adsorption depends on process conditions such as temperature and pH and process design factors such as carbon/wastewater contact time and the number of the carbon columns. If performed under the right conditions, activated carbon adsorption can be an effective treatment technology for PFPR industry wastewaters. Carbon adsorption capacity depends on the characteristics of the adsorbed compounds, the types of compounds competing for adsorption, and characteristics of the carbon itself. If several constituents that are amenable to activated carbon adsorption are present in the wastewater, they may compete with each other for carbon adsorption capacity. This competition may result in low adsorption or even desorption of some constituents.

Activated carbon comes in two sizes: powdered carbon has a diameter of less than 200 mesh, while granular carbon has a diameter greater than 0.1 millimeter. Granular carbon is more commonly used in wastewater treatment; powdered carbon is used less frequently because the small particle size creates regeneration and design problems. Activated carbon is obtained from vendors in bulk or in a variety of container sizes. At smaller facilities, the container in which the carbon is sold is intended to be used as the carbon bed, with influent wastewater passing into one end of the container and treated effluent water passing out of the opposite end. At larger facilities, carbon is purchased and added to a column that is installed at the facility.

Carbon is regenerated by removing the adsorbed organic compounds through steam, thermal, or physical/chemical methods. Thermal and steam regeneration are the most common methods to regenerate carbon used for wastewater treatment. These methods volatilize the organic compounds that have adsorbed onto the carbon. Afterburners are required to ensure destruction of the organic vapors; a scrubber may also be necessary to remove particulates from the air stream. Physical/chemical regeneration uses a solvent, which can be a water solution, to remove the organic compounds. Carbon is usually shipped back to the vendor for regeneration, although some facilities with larger carbon beds may find it economical to regenerate carbon on site.

Chemical Oxidation



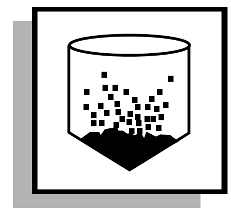
Chemical oxidation modifies the structure of pollutants in wastewater to similar, but less harmful, compounds through the addition of an oxidizing agent. During chemical oxidation, one or more electrons transfer from the oxidant to the targeted pollutant, causing its destruction.

One common method of chemical oxidation, referred to as alkaline chlorination, uses chlorine (usually in the form of sodium hypochlorite) under alkaline conditions to destroy pollutants such as cyanide and some pesticide active ingredients. However, facilities treating wastewater using alkaline chlorination should be aware that the chemical oxidation reaction may generate toxic chlorinated organic compounds, including chloroform, bromodichloromethane, and dibromochloromethane, as byproducts.

Adjustments to the design and operating parameters may alleviate this problem, or an additional treatment step (e.g., steam stripping, air stripping, or activated carbon adsorption) may be required to remove these byproducts.

Chemical oxidation can also be performed with other oxidants (e.g., hydrogen peroxide, ozone, and potassium permanganate) or with the use of ultraviolet light. Although these other methods of chemical oxidation can effectively treat PFPR wastewaters, they typically entail higher capital and/or operating and maintenance costs, greater operator expertise, and/or more extensive wastewater pretreatment than alkaline chlorination. Additional information about these other methods can be found in the Final PFPR Technical Development Document (EPA 821-R-96-019).

Chemical Precipitation



Chemical precipitation is a treatment technology in which chemicals (e.g., sulfides, hydroxides, and carbonates) react with organic and inorganic pollutants present in wastewater to form insoluble precipitates. This separation treatment technology is generally carried out in the following four phases:

1. Addition of the chemical to the wastewater;
2. Rapid (flash) mixing to distribute the chemical homogeneously throughout the wastewater;
3. Slow mixing to encourage flocculation (formation of the insoluble solid precipitate); and
4. Filtration, settling, or decanting to remove the flocculated solid particles.

These four steps can be performed at ambient conditions and are well suited to automatic control.

Hydrogen sulfide or soluble sulfide salts (e.g., sodium sulfate) are chemicals commonly used in the PFPR industry during chemical precipitation. These sulfides are particularly effective in removing complexed metals and heavy metals (e.g., mercury, lead, and silver) from industrial wastewaters. Hydroxide and carbonate precipitation can also be used to remove metals from PFPR wastewaters, but these technologies tend to be effective on a narrower range of contaminants.

Hydrolysis

OH^-

Hydrolysis is a chemical reaction in which organic constituents react with water and break into smaller (and less toxic) compounds. Basically, hydrolysis is a destructive technology in which the original molecule forms two or more new molecules. In some cases, the reaction continues and other products are formed. Because some pesticide active ingredients react through this mechanism, hydrolysis can be an effective treatment technology for PFPR wastewater.

The primary design parameter considered for hydrolysis is the half-life, which is the time required to react 50% of the original compound. The half-life of a reaction generally depends on the reaction pH and temperature and the reactant molecule (e.g., the pesticide active ingredient). Hydrolysis reactions can be catalyzed at low pH, high pH, or both, depending on the reactant molecule. In general, increasing the temperature increases the rate of hydrolysis.

Identifying the best conditions for the hydrolysis reaction results in a shorter half-life, thereby reducing both the size of the reaction vessel required and the treatment time required. A more thorough discussion of hydrolysis of pesticide active ingredients can be found in the *Final Pesticides Formulators, Packagers, and Repackagers Treatability Database Report* (DCN F7185) or the Final Pesticide Manufacturing Technical Development Document (EPA-821-R-93-016 or DCN F6442).

Other Treatment Technologies

In addition to the technologies listed above, a variety of other technologies effectively treat PFPR wastewater, including reverse osmosis and ultraviolet light assisted ozonation. Although these technologies are not discussed here, additional information on the treatment tests conducted by EPA can be found in the Final PFPR Technical Development Document (EPA 821-R-96-019) and in the administrative record supporting the final PFPR rulemaking.

Additional Treatability Documents (available through EPA's Office of Water)

General References

Development Document for Best Available Technology, Pretreatment Technology, and New Source Performance Technology for the Pesticide Formulating, Packaging, and Repackaging Industry—Final, EPA 821-R-96-019, September 1996

Development Document for Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards for the Pesticide Chemicals Manufacturing Point Source Category, EPA 821-R-93-016, September 1993 (DCN F6442)

Final Pesticides Formulators, Packagers, and Repackagers Treatability Database Report, March 1994 (DCN F7185)

Pesticide Formulators, Packagers, and Repackagers Treatability Database Report Addendum, September 1995 (DCN F7700)

Pilot-Scale Tests of the Universal Treatment System for the Pesticides Formulating, Packaging, and Repackaging Industry, September 1996 (DCN F7938)

Evaluation of the Universal Treatment System of Pesticide Formulator/Packager Wastewater, September 1993 (DCN F6446)

Membrane Technologies

Membrane Filtration Treatability Study, July 1991 (DCN F5541)

Membrane Separation Study for the Pesticide Formulator Packager Project, January 1994 (DCN F6445)

Final Pilot-Scale Membrane Separation Study, August 1996 (DCN F7939) Hydrolysis

Hydrolysis

Treatability of PAIs by Hydrolysis - Bench-Scale Tests, November 1990 (DCN F5544)

Hydrolysis Treatability Field Study, September 1990 (DCN F5546)

Pyrethrin Wastewater Treatability Report, June 1993 (DCN F6167)

Activated Carbon

Activated Carbon Isotherms for Pesticides, October 1989 (DCN F5885)

Accelerated Column Testing - Pesticide Manufacturing Wastewaters - Phase 2, September 1991 (DCN F5884)

Carbon Adsorption Isotherms for Toxic Organics, April 1980 (DCN F5786)

Emulsion Breaking

Emulsion Breaking Performance Study - Final Report, August 1996 (DCN F7937)

Note: These documents can be found in the administrative record supporting the final PFPR rulemaking, which can be accessed through EPA's Office of Water. The EPA Water Docket is open from 9 a.m. to 3:30 p.m. and can be reached at (202)260-3027. The document control number (DCN) is included in parentheses at the end of the reference. Reasonable fees may be charged for copying.

See Chapter 9 for a list of contacts.